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Development of Chrome Yellow

Glazes at low Temperatures

Ceramics

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DEVELOPMENT OF CHROME YELLOW GLAZES

AT

LOW TEMPERATURES

BY

RALPH RAYMOND DANIELSON

THESIS

FOR THE

Degree of

BACHELOR OF SCIENCE

IN CERAMICS

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May 30, 1914

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Ralph Raymond Danielson

ENTITLED Development of Chrome Yellow Glazes at Low

Temperatures

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Ceramics

R J Stull

Instructor in Charge

APPROVED: R J Stull

HEAD OF DEPARTMENT OF Ceramics

291737

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Development of Chrome Yellow Glazes at Low Temperatures.

Yellow glazes may be produced by the addition of Fe, Ur, or Sb compounds to an otherwise colorless glaze. However, the results obtained from these coloring agents are rather unsatisfactory. Iron gives a yellow but the range of color is very short, tending toward a brown with .03 mols. of FeO. The color is either straw yellow or brown and is obtained in high fired glazes with better results than in low fired glazes.

Iron and antimony compounds are also used to give a yellow but are unreliable. Over-firing or a long burn will bleach the color. Furthermore a primary yellow can not be obtained with either one of the these substances.

Uranium gives a yellow but is rather expensive except for the higher grades of pottery. In a glaze high in lead with uranium an orange is obtained, but in a high fired glaze a lemon yellow is obtained. High fired glazes with uranium are unreliable.

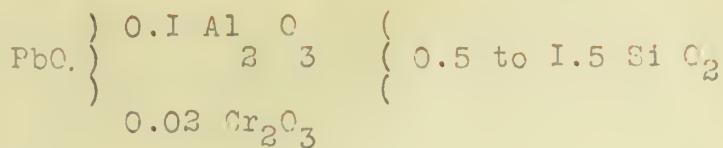
In the work done by Rand and Hornung,³ it was found that glazes containing chromium within the following range of composition gave colors approaching yellow instead of the I. F. H. Riddle ^{1, 2} Coloring Power of Uranium Oxide Trans. Am. Ceramic Society Vol. 8 P. 210

2. R. L. Minton Discussion on Uranium Oxide
T. A. C. S. Vol. 9 P. 277

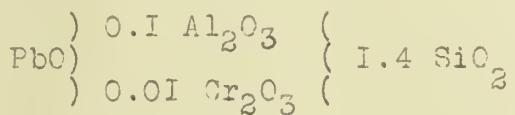
3. Rand & Hornung Chromium Colors at Low Temperatures.

Thesis for Degree of B. S. in Ceramics
University of Illinois-1913.

customary reds and greens.



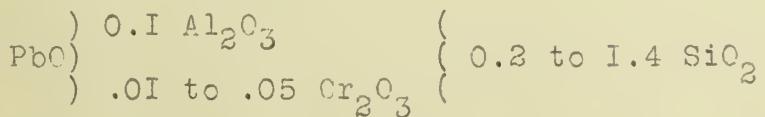
Although Rand and Hornung did not develop true yet low colors, they obtained orange, which suggested the possibility of a chrome yellow glaze at low temperatures. No data on chrome yellow glazes except that given by Rand and Hornung could be obtained. Accordingly, the following empirical formula from the work of Rand and Hornung was used as a basis for constructing a glaze group.



The above formula gave the glaze highest in SiO_2 and Cr_2O_3 from which orange was obtained.

Group I.

In this group the RO and Al_2O_3 remain constant, the SiO_2 and Cr_2O_3 being variables. The limits covered were:



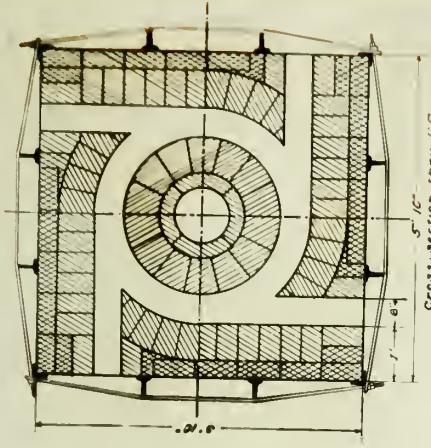
Twenty five glazes were made, the horizontal series being designated by letters and the vertical series by numbers. The members of the group were made by blending the four corner glazes according to their combining weights. The formulae and batch weights of the four corners are:

| Glaze No. | PbO | Formulae | | | Batch Weights | | | | |
|--------------|-----|--------------------------------|--------------------------------|------------------|---------------|------------------|--------------------------------|-------|--|
| | | Al ₂ O ₃ | Cr ₂ O ₃ | SiO ₂ | White lead | Chine Clay, 7 | Cr ₂ O ₃ | Flint | |
| IAI | I | 0.1 | .01 | 0.2 | 357.7 | 25.8 | 1.53 | 0.0 | |
| IA5 | I | 0.1 | .01 | 1.4 | 357.7 | 25.8 | 1.53 | 73.0 | |
| IFI | I | 0.1 | .05 | 0.2 | 357.7 | 25.8 | 7.65 | 0.0 | |
| IE5 | I | 0.1 | .05 | 1.4 | 357.7 | 25.8 | 7.65 | 73.0 | |

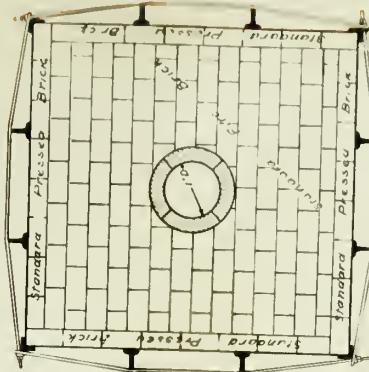
The four batches were made from materials passed thru a 30-mesh sieve, ground wet for two hours and passed thru a 120-mesh sieve. The glazes were blended by weight and applied to biscuit tile.

One set of trials was dipped thick and another set dipped thin. There was some cracking of the glaze after drying, especially on the thickly dipped pieces. The trials were placed in saggers and burned in an open fire down draft oil fired kiln (Fig. I) in about five hours. The temperature was carried up at a rate of about 200° an hour. A platinum-rhodium couple was used with a Siemens Halske high resistance galvanometer, the temperature being read directly on the instrument. When Seger cone 09 was about half down, (approximately 970° C) the oil burners were shut off and the kiln allowed to cool slowly for about twelve hours to 300° C. Then the kiln crown was raised and cooling allowed to proceed rather quickly to room temperature.

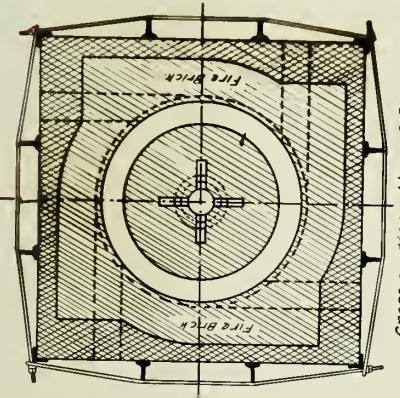
Most of the glazes were red or tending toward a red brown, although in some of the glazes low in chromium there were



Cross-section thru E/F



Cross-section three 67



Cross-section thru C-2 showing opening into flue.

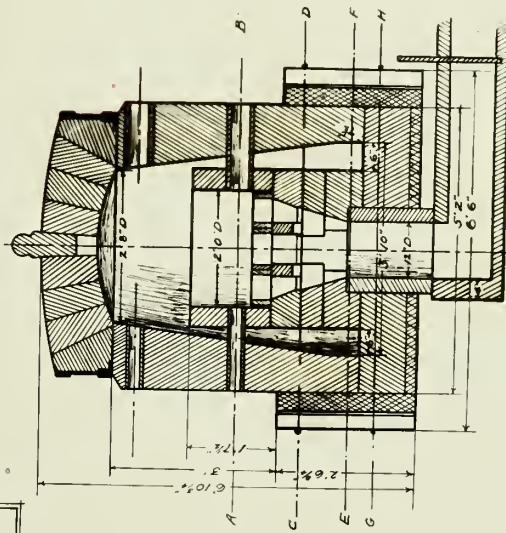
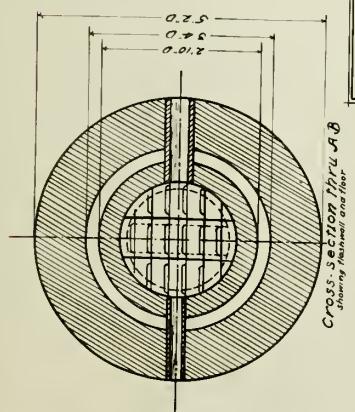
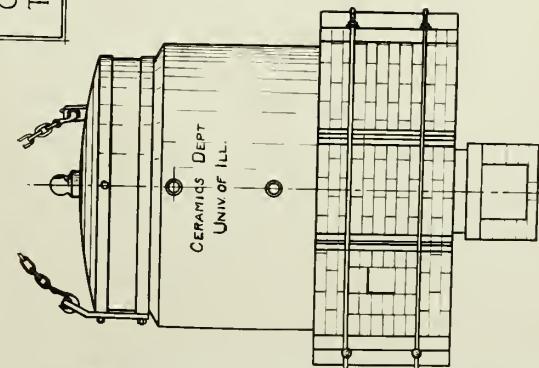


FIG. 1.



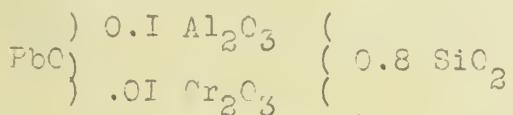
Cross-Section thru A-B
showing Hatchwall and floor



OIL FIRED
TEST KILN

4.

yellow spots where the glaze was comparatively thin. All glazes containing 0.3 mols. of SiO_2 were matt and were under-fired. The glazes with 0.5 mol. SiO_2 developed small crystals. P-3 was a good cherry red in color. The glazes containing 1.4 mols. SiO_2 were red brown with some spots of green and were somewhat under-fired. A-3 of the following formula gave a glaze, orange in color, which was the nearest approach to the yellow of any member of the group.



An attempt has been made to describe the color and texture of the individual glazes (Fig. 2). The following conclusions can be drawn from the work in group I.

Increasing Cr_2O_3 or decreasing SiO_2 or both gave increasing red. Decreasing Cr_2O_3 or increasing SiO_2 , or both, gave decreasing red and increasing yellow.

It was observed that .01 Cr_2O_3 was above the maximum limit for the yellow since this amount gave orange with high SiO_2 and red with low SiO_2 .

The glazes were slightly crazed as might be expected since they were comparatively high in PbO and low in SiO_2 .⁴

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4. W. M. Fickes The Permissible Variations in the Silica and Alumina Contents of Raw Lead Glazes.

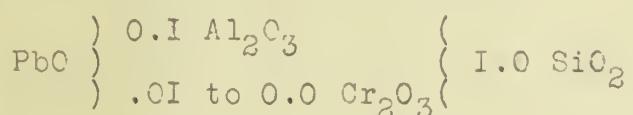
| | 1. | 2. | 3. | 4. | 5. |
|----|-------------------------------|-------------------------------------|--------------------------------------|-----------------------------------|---------------------------------------|
| F. | Dark red Matt Underfire | Park red Crystal- | Red Underfired | Red Underfired Crystals | Red brown Underfired |
| D. | " | Red Large crystals | Good red Matt | Red Crystals | Red brown Immature |
| C. | " | Red Crystals | Good red | Red Matt | Red Immature |
| B. | " | Red Crystals Immature | Red Orange on edges. crazed | Red Immature | Brown Immature |
| A. | Dark red Matt Immature | Orange red Crystals Crazed | Orange yellow crazed | Yellow brown Matt crazed | Yellow brown Immature crazed |

FIG. 2

15.

Series A.

Since the results of Group I indicated that Cr_2O_3 should be less than .01 mols. and SiO_2 above 0.8 mole, in order to approach the yellow, Series A was designed in which the Cr_2O_3 diminished from .01 to 0.0 mols. with constant SiO_2 at 1.0 mol. The limits covered in this series are:



Ten glazes were made in this series, the individual members being designated by numbers. The members were made by blending the two end members. The formulae and batch weights of the two end members are:

| Glaze No. | Formulae | | | | | Batch weights | | | |
|--------------|----------|-------------------------|----------------|-------------------------|---------------|---------------|-------|-------------------------|--|
| | PbO | Al_2O_3 | SiO_2 | Cr_2O_3 | White lead | Clay | Flint | Cr_2O_3 | |
| I-A | 1.0 | 0.1 | 1.0 | .01 | 258.0 | 25.8 | 48.0 | 1.53 | |
| IO-A | " | " | " | .00 | " | " | " | 0.0 | |

The clay used was half Tenn. ball #7 and half N. C. Kaolin. The ball-clay was used to prevent flaking of the glaze.

First Burn. The glazes were applied to white ware tile and burned to Cone 05, the point of maturity of the glazes being determined by draw trials. A set of Series E and C were also burned at this time with Series A in the oil fired kiln.

The color and texture of the several glazes are described in the following table:

Series A----Cone 05

Series A--- Cone 05

I-A. Yellow brown----high gloss----crazed

Intervening members decreasing in intensity of color from the yellow brown of I-A to a very pale yellow in IC-A. All members showed a high gloss.

Second Burn. The glazes had been allowed to settle before the second burn was made so that some of the Cr_2O_3 was not thoroly disseminated in the glaze. However the general results were good, the glazes being fired to Cone 02. The glazes were burned in a gas fired kiln(Fig. 3) in three and one half hours.

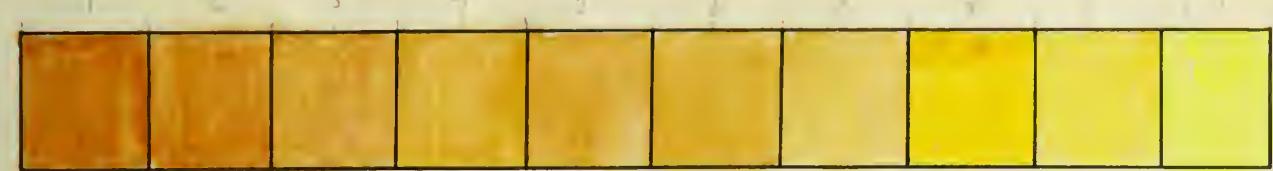
The results are given in the following table:

Series A----Cone 02

| | | | |
|------|---------------|------------|-----------------|
| 2-A | Dark yellow | High gloss | Good texture |
| 3-A | " | " | " |
| 4-A | Amber | " | " |
| 5-A | " | " | Slightly crazed |
| 6-A | Light yellow | " | Good texture |
| 7-A | Lemon yellow | " | " |
| 8-A | " | " | " |
| 9-A | Pale yellow | " | " |
| IC-A | Straw yellow* | " | " |

.....

* This glaze was probably colored by chromium fumes, since it is a well known fact that Cr_2O_3 is volatile at kiln temperatures.



Color Chart
Series A--Cone 05



Color Chart
Series A-- Cone 02

I. 2. 3.



Color Chart

Group I. Cone05

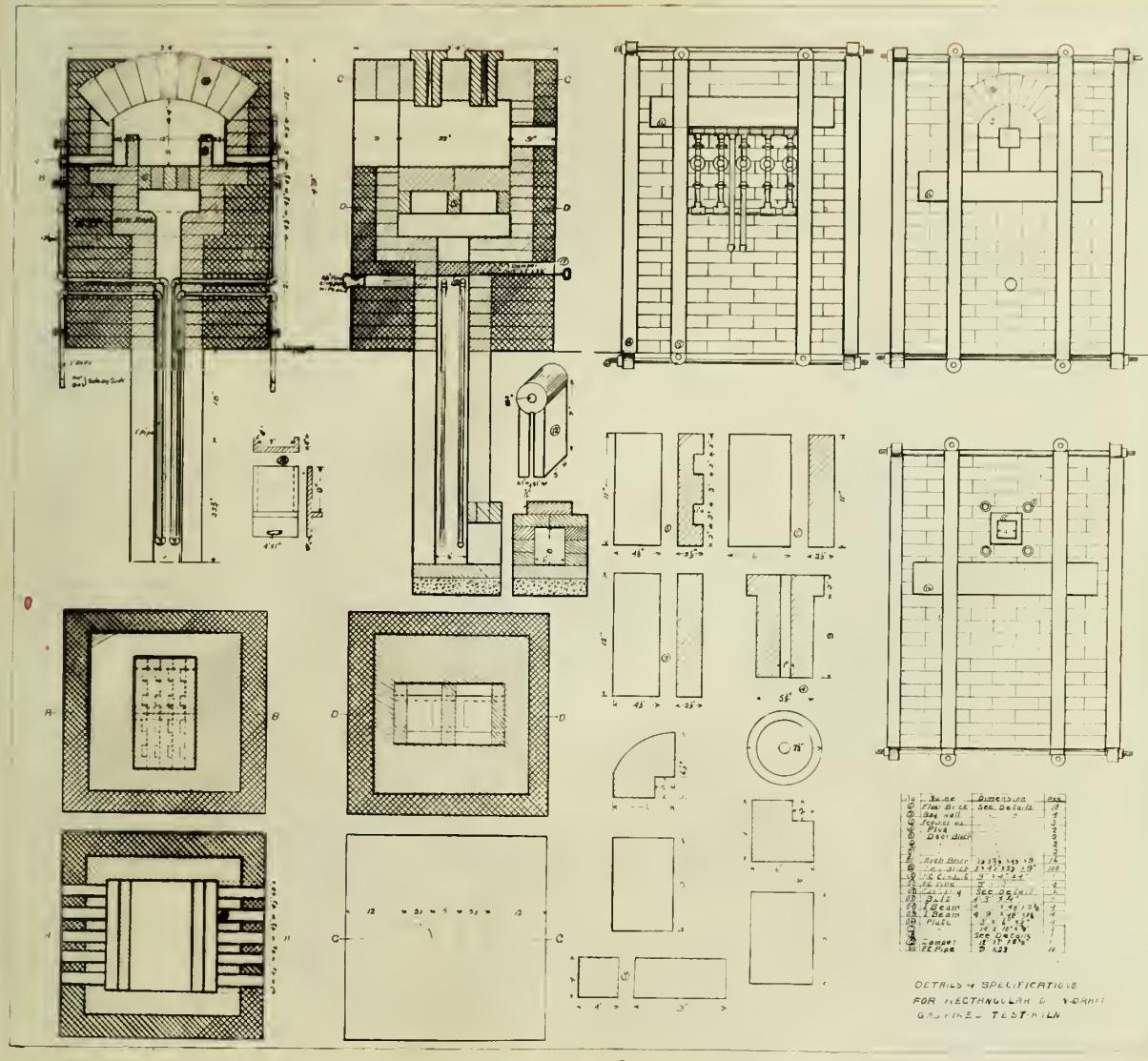
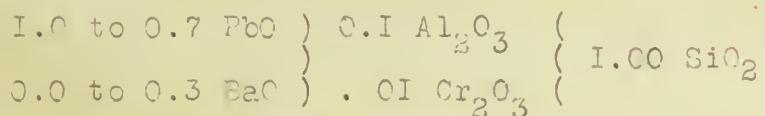


FIG. 3

Series B

This series was designed to show the effect on color of replacing part of the PbO with BaO, the SiO₂ and P₂O₅ remaining constant. The limits covered are:



Ten glazes were also made in this series, I-E having the same composition as I-A. The formulae and batch weights of the end members are:

| Glaze No. | Formulae | | | | | Batch Weights | | | | |
|--------------|----------|-----|--------------------------------|--------------------------------|------------------|---------------|-------------------|----------------------|--------------------------------|------|
| | PbO | BaO | Al ₂ O ₃ | Cr ₂ O ₃ | SiO ₂ | White lead | PbCO ₃ | ClaySiO ₂ | Cr ₂ O ₃ | |
| I-B | I.O | O | .I | .0I | I.O | 258 | 0 | 25.8 | 48 | I.53 |
| IO-B | 0.7 | .3 | " | " | " | 180.6 | 59 | " | " | " |

Equal parts of ball clay and China clay were used as in Series A. The glazes were applied to white ware tile and burned as described in the discussion on Series A.

Series B---- Cone 05

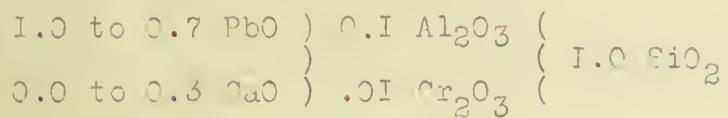
| | | | | | | | | | | |
|------|-------------------|-----------------|--------|------------|---|--|--|--|--|--|
| I-B | Same glaze as I-A | | | | | | | | | |
| 2B | Brown----- | high gloss----- | crazed | | | | | | | |
| 3-B | " | matt | | underfired | | | | | | |
| 4-B | Light brown | " | | | " | | | | | |
| 5-B | " | " | | | " | | | | | |
| 6-B | Yellow brown | " | | | " | | | | | |
| 7-B | Yellow | " | | | " | | | | | |
| 8-B | Light yellow | " | | | " | | | | | |
| 9-B | " | " | | | " | | | | | |
| IO-B | " | " | | | " | | | | | |

Series E---Cone 02

| | | | |
|------|--------------|-----------------|-----------------|
| 3-E | Brown----- | good gloss----- | Slightly crazed |
| 3-F | Light brown | fair " | " " |
| 4-E | " " | " " | " " |
| 5-E | " " | semi-matt | " " |
| 6-E | " " | " | " " |
| 7-E | " " | " | Underfired |
| 8-E | Yellow | matt | " |
| 9-F | Light yellow | " | " |
| 10-E | " " | " | " |

Series C.

Series C was designed to show the effect on color of replacing part of the PbO with CaO, the SiO_2 and P_2O_5 remaining constant. The limits covered are:



Ten glazes were made as in Series A and B, I-C having the same composition as I-A. The formulae and batch weights of the end members are:

| Glaze No. | Formulae | | | | | Patch weights | | | | | |
|--------------|----------|-----|--------------------------------|--------------------------------|------------------|---------------|------|-------------------|------|------------------|--------------------------------|
| | PbO | CaO | Al ₂ O ₃ | Cr ₂ O ₃ | SiO ₃ | White | lead | CaCO ₃ | Clay | SiC ₂ | Cr ₂ O ₃ |
| I-C | 1.0 | 0.0 | 0.1 | | .01 | 1.0 | 258 | 0 | 25.8 | 48 | 1.53 |
| IC-C | .7 | .3 | " | " | " | 180.6 | 30 | " | " | " | " |

The color and texture of the individual glazes are described below:

Series 2 --- Cone 05

I-C Dark yellow tending toward brown-- high gloss-- crazed

| | | | | | | |
|------|--------------|--------|---|-------------------------|---|---|
| 2-C | " | " | | " | " | " |
| 3-C | Similar | to I-C | | | | |
| 4-C | " | " | " | | | |
| 5-C | " | " | " | | | |
| 6-C | " | " | " | | | |
| 7-C | " | " | " | but slightly underfired | | |
| 8-C | Yellow | | | " | | |
| 9-C | " | | | " | | |
| 10-C | Light yellow | | | " | | |

The results obtained were rather unsatisfactory as the glazes were all underfired.

Series C--- Con. 92

| | | | |
|-----|----------------|-------------------|-----------------|
| I-C | Dark yellow | good glaze | rich gloss |
| 3-C | Similar to I-C | | |
| 3-C | " " " | | |
| 4-C | " " " | | |
| 5-C | " " " | | |
| 6-C | Amber | " " | " " |
| 7-C | Similar to 6-C | | |
| 8-C | Light yellow | high gloss | slightly crazed |
| 9-C | " " | decrease in gloss | unfired |

Conclusions

The best yellows are obtained with .003 to .008 molecules of Cr_2O_3 .

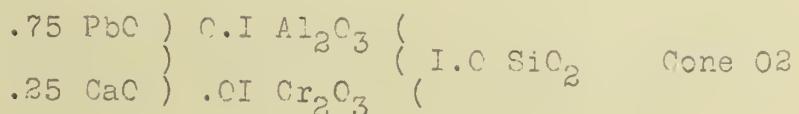
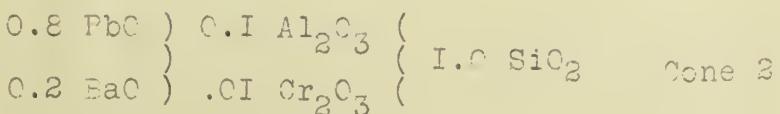
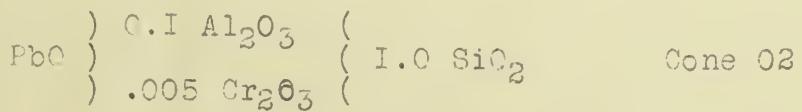
Increase of CaO makes glaze more refractory and decreases intensity of color.

Increase of BaO makes glaze more refractory but changes color to a greenish yellow.

Decreasing Cr_2O_3 decreases intensity of color.

Increasing temperature of burning decreases crazing while thick dipping increases the crazing.

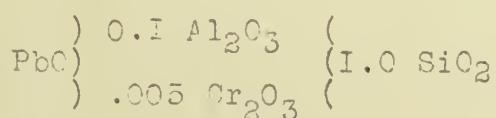
The best yellows are found in glazes of the following composition:



W. L. Brown,⁵ in his work on lead chromate as an indicator for acid and basic fluxes, claims that the basic lead chromate ($PbO \cdot Cr_2O_3$, PbO) gives a red color while the neutral chromate ($PbO \cdot CrO_3$) gives yellow. There is no acid chromate of lead formed, but the green color of a chromium glaze is probably due to undissolved chromium oxide (Cr_2O_3). That this is true was shown in Group I. The glazes high in SiO_2 were under-fired and were spotted green or tending toward a green color. The SiO_2 did not have opportunity to exert its full influence as a solvent. Consequently, the green color of the undissolved Cr_2O_3 predominated.

The development of the red color is shown in Group I, A-3 to F-3. In this series the acid content is constant with an increase in the basic content (Cr_2O_3) and the color is seen to change from an orange to a deep red color. In fact any series in this group having constant SiO_2 and increasing Cr_2O_3 intensifies the red color.

A type formula for a yellow glaze might be given as follows:



The above formula gives an oxygen ratio (ratio of atoms of oxygen in SiO_2 to number of atoms of oxygen in the RC and R_2O_3 combined) of 1.5 and a molecular ratio of SiO_2 to Al_2O_3

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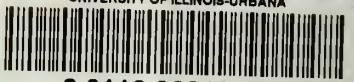
5. W. L. Brown Notes on the Use of Chromate of Leads as an Indicator for Acid and Basic Fluxes.

of about 1,0. The oxygen ratio and molecular ratio calculated for several yellow glazes gave approximately the above figures. Therefore, a raw lead chromium glaze with the above oxygen and molecular ratio ought to give a yellow glaze. Decreasing the O. R. and M.R. or decreasing acidity tends toward a red color, although a very large decrease in SiO_2 will tend toward a green color due to undissolved chromium and an acid glaze.





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